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THE QUESTION OF ATMOSPHERIC CORROSION OF POWDERED COPPER

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In the literature of recent years, atmospheric corrosion is treated as a special type of electrochemical corrosion, and it is assumed that the corrosive processes take place beneath the film of moisture on the borderline of the metal surface and the liquid phase (1).

One usually sets the temperature limits of atmospheric corrosion within the bounds of existence of water in the liquid state. The corrosive action of dry vapors and gases on metals (chemical corrosion) is considered possible at temperatures much higher than the boiling point of water -- over 200 degrees Centigrade for chlorine, over 300 degrees Centigrade for ^{hydrogen chloride} ~~chlorine~~ ^{hydrogen chloride} and over 450-500 degrees Centigrade for ^{SO₂} ~~sulfur~~ ^{gas} and hydrogen sulfide (2). But even in this case, when corrosion takes place in an atmosphere of dry vapors and gases (of hydrogen sulfide for instance), one generally assumes that here, too, the process takes place with the participation of moisture forming through the interaction between the attacking substance and the metal or the oxide film.

Thus, the presence of moisture is considered indispensable to atmospheric corrosion.

According to the film theory of Kistjakovskiy, atmospheric corrosion is considered to be an intermediate stage between purely

chemical and electrochemical processes. The process of corrosion consists of three phases:

1. Interaction between metal and moist oxygen with the formation of metal oxide films.
2. Solidification of films (coagulation, the formation of crystallites).
3. Adsorption of gases, condensation of liquids, and colloido-electrochemical processes (3).

The destruction of the original film (the appearance of ^{centers} areas of solidification) may be ^{induced} provoked by particles suspended in air, vapors and gases. Evidently, in this theory too, the influence of water is decisive, but the process of corrosion as a whole is not ^{explained exclusively by} reduced exclusively to the level of electrochemical reactions between the surface of the metal and the moisture film.

The study of corrosion of metals in powder form, where atmospheric corrosion assumes a specific character and certain of its aspects appear to be clearer than with compact metals, provides better insight into the mechanisms of atmospheric corrosion.

Experiments conducted on corrosion of copper powder in an atmosphere of various aggressive gases have demonstrated ^{that} the moisture is the principal controlling factor in the corrosive process (4). Starting from there we have evolved an original method of stabilizing copper powders against corrosion; the method consists in the hydrophobization of the metal particle surfaces (5).

With the creation of chemiadsorbed hydrophobic films we prevent the adsorption of water vapors by the surfaces of the metal particles, and consequently we wholly eliminate the possibility of the formation of adsorption films of moisture.

The resistance to corrosion of a metal in powder form increases considerably this way. For instance, in an atmosphere of carbon dioxide saturated with water vapor at 40 degrees Centigrade, the resistance increases from 50 to 70 times. Such a high resistance against atmospheric corrosion is understandable since the flow of electrochemical reactions is impossible in the case of these stabilized metal powders.

In the present experiment we have endeavored to study and compare qualitatively the corrosive behavior of hydrophobic and common copper in powder form.

EXPERIMENTAL SECTION

(Technicians T. A. Tkachenko and K. V. Mityushina took part in the experimental part of this work)

The procedures followed in the corrosion experiments were basically similar to those of previous tests (4). The corrosion tests were conducted in ^{desiccators} ~~exsiccators~~ with a capacity of 2 liters. To insure complete uniformity in experimental conditions, two portions of powder were placed in each ^{des} ~~exsiccator~~, one hydrophobic, the other common. The tests were conducted in an atmosphere of hydrogen sulfide, ^{hydrogen chloride} ~~chlorine hydride~~, ammonia, and carbon dioxide. The gases were passed through ^{flasks with} ~~jars of~~ calcium chloride and sulfuric acid in order

to dry them. In certain cases ^{flasks with} ~~jars of~~ soda lime were added. In filling the ^{des} exsiccators the same amounts of gas were always used, and identical procedure was followed. The tests were conducted on copper powder of factory make. The extent of corrosion was established according to weight increase.

The results are given in Tables I and II.

Table I

Extent of Corrosion of Copper Powder in Atmospheres
of Hydrogen Sulfide and Carbon Dioxide

(Exposure 8 Hours, Temperature 40 ± 1 degrees Centigrade)

Type of Powder	Corrosive Atmosphere			
	Hydrogen Sulfide	Carbon Dioxide	Water Vapors	
Common	7.72	28.22	0.05	0.72
Hydrophobic	4.21	6.56	0.05	0.04
				0.33
				0.002

(Note: In Table I and following the amount of weight increase is expressed in percentages of the original specimen weight.)

Table II

Degree of Corrosion of Copper Powder in
Atmospheres of Chlorine Hydride and Ammonia

(Exposure, 4 hours; Temperature, 40 degrees Centigrade)

Type of Powder	Corrosive Atmosphere		
	Chlorine Hydride		Ammonia
	Dry	Saturated with water vapor	
Common	3.01	2.09	4.00
Hydrophobic	1.90	1.02	0.73

(Note: The ammonia atmosphere was created by introducing into the exsiccator of a small amount of a 25 percent solution of ammonia.)

As follows from Tables I and II, hydrophobic powders are always less subject to corrosion than the common powders. In moist atmospheres of Hydrogen sulfide and carbon dioxide the corrosion of common copper increases substantially, while in the case of hydrophobic metal it either does not change (CO_2 atmosphere), or changes insignificantly (H_2S atmosphere). In an atmosphere of chlorine hydride we note an anomaly in the conduct of copper powder. Here the corrosion of the metal appears to be more intense in a dry gaseous atmosphere than in the presence of water vapor. We will explain this anomaly later.

We then conducted experiments of powder corrosion in an atmosphere of hydrogen sulfide during a more prolonged period of time. The results are presented in Table III.

Table III

Corrosion of Copper Powder in an Atmosphere of Hydrogen
Sulfide and in relation to the length of exposure time

(Temperature + 16 ± 2 degrees Centigrade)

Experiment Number	Type of Powder	Corrosion Atmosphere	Exposure (in Hours)		
			24	48	264
1	Common	Dry H ₂ S	16.1	16.2	20.5
2	Hydrophobic		6.5	6.9	15.2
3	Common	H ₂ S saturated with water vapors	18.8	18.1	20.0
4	Hydrophobic		12.2	10.0	17.6
5	Common	H ₂ S saturated with water vapors, and water saturated with H ₂ S	-	20.6	-
6	Hydrophobic		-	12.2	-

Apparently, the principal mass of non-hydrophobic copper is corroded immediately, during the initial period. Later the process of corrosion continues only in the depth of the specimen. Table III also shows that hydrophobic copper is corroded considerably more slowly than common copper. However, the extent of corrosion grows in time. The concentration of gas in the reaction is very highly important. For instance, in experiments 5 and 6 (Table II) small glasses containing water previously saturated with hydrogen sulfide were used, while in experiments 3 and 4 common distilled water was used. This led to a lower concentration of gas in experiments 3 and 4 because of the partial absorption of the hydrogen sulfide by the water and, as a consequence, it led to a reduction in the extent of corrosion.

As we know, metal powders stabilized by means of soap are not wetted by water. But still more interesting results were obtained with regard to the wettability of portions previously used in corrosion experiments. It developed that previously hydrophobized copper powders retained the property, being unwettable by water even after prolonged atmospheric corrosion.

It was noticed further that powder samples caked after corrosion tests. Common powders caked to a greater degree than the hydrophobic powders. Especially pronounced caking was observed in non-hydrophobic powders in the presence of water vapor. However, when corrosion took place in moist atmosphere, but under higher temperatures (90 degrees Centigrade), the corroded samples of powder caked considerably less compactly than under lower temperatures.

Moreover the difference in caking between common and hydrophobic powders was not observed under these conditions. Consequently, under normal temperatures, water has a substantial influence on the caking process -- it facilitates, apparently, a closer contact and relationship of the metal particles among themselves.

The corrosion tests of hydrophobic copper powder in atmospheres of hydrogen sulfide, chlorine hydride, and ammonia doubtless testify to the presence of atmospheric corrosion even in the absence of the moisture film on the surface of the highly dispersed particles of metal. Apparently the corrosion process is the result of a direct interaction between gases and vapors and the surface of the metal.

The relatively higher degree of corrosion in an atmosphere of dry hydrogen sulfide of common copper in powder form as compared to

the hydrophobic powder, can be explained as follows: First, in the case of unprotected powders, the complete surface of the particles is accessible to the action of gases, whereas in the presence of hydrophobic films over the metal surface, the gas must surmount a certain resistance of the protective film in order to make direct contact with the metal. Second, the water formed as a result of the interaction between hydrogen sulfide and the metal will be adsorbed by the common powder and will favor the appearance of an electrochemical corrosion in addition to the chemical one. It is self-evident that in the case of hydrophobic powders this possibility is excluded. A similar picture appears in even stronger light when the reaction atmosphere is saturated with water vapor, in which case the corrosion of a non-hydrophobic metal increases considerably. Here we have the formation of a moisture film not only as a consequence of a chemical interaction between hydrogen sulfide and the metal, but also as a result of adsorption and capillary condensation on the highly-dispersed metal particles. It is quite understandable that in addition to the chemical corrosion we have here a very intensive electrochemical corrosion as well.

As follows from the experimental data, under similar conditions the corrosion of copper powder either does not change at all in practice, or else changes very insignificantly. A certain intensification of hydrophobic metal powder corrosion in the presence of water vapor can be explained by the latter's softening action on the film formed by the products of reaction between the metal and hydrogen sulfide. The lower degree of copper powder corrosion in an atmosphere of chlorine hydride saturated with water vapor in comparison with the dry gas

is caused by the reduced concentration of the aggressive gas after its partial absorption by the water.

CONCLUSIONS

1. With hydrophobic copper we show the possibility of atmospheric corrosion in the absence of a moist film on the corroded surface. In connection with this we express an opinion about the faultiness of indiscriminately assuming atmospheric corrosion to be a special type of electrochemical corrosion.

2. In the temperature range corresponding to the liquid state of water, a purely chemical -- gaseous -- corrosion plays a role substantially paralleling that of electrochemical corrosion.